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Crystal structure of trihydrogen bis{[1,1,1-tris(2-oxidoethylaminomethyl)ethane]cobalt(III)} trinitrate

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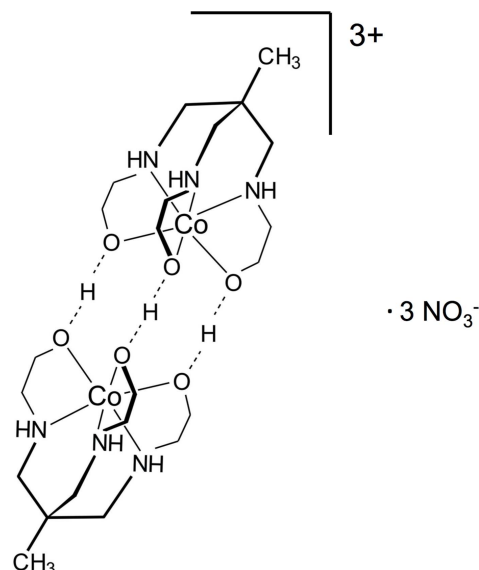
The title compound, $[\text{Co}_2(\text{L})_2]^{3+} \cdot 3\text{NO}_3^-$ [where $\text{L} = \text{CH}_3\text{C}(\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}_{1/2})_3$], has been synthesized from the ligand 1,1,1-tris(2-hydroxyethylaminomethyl)ethane. The cobalt(III) dimer has an interesting and uncommon $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen-bonding motif with the three bridging hydroxy H atoms each being equally disordered over two positions. In the dimeric trication, the octahedrally coordinated Co^{III} atoms and the capping C atoms lie on a threefold rotation axis. The N atoms of two crystallographically independent nitrate anions also lie on threefold rotation axes. $\text{N} \cdots \text{H} \cdots \text{O}$ hydrogen bonding between the complex cations and nitrate anions leads to the formation of a three-dimensional network structure. The compound is a racemic conglomerate of crystals containing either D or L molecules. The crystal used for this study is a D crystal.

Keywords: crystal structure; cobalt(III) complex; 1,1,1-tris(2-hydroxyethylaminomethyl)ethane; hydrogen-bonding motif; racemic conglomerate.

CCDC reference: 1443816

1. Related literature

For the crystal structure of the related *cis*-aqua-hydroxido complex of chromium(III), see: Ardon *et al.* (1987).



2. Experimental

2.1. Crystal data

$[\text{Co}_2(\text{C}_{11}\text{H}_{25.5}\text{N}_3\text{O}_3)_2](\text{NO}_3)_3$
 $M_r = 799.57$
 Trigonal, $R32$
 $a = 8.543$ (4) Å
 $c = 39.11$ (2) Å
 $V = 2472$ (3) Å³

$Z = 3$
 Mo $K\alpha$ radiation
 $\mu = 1.09$ mm⁻¹
 $T = 122$ K
 $0.31 \times 0.25 \times 0.15$ mm

2.2. Data collection

Bruker APEXII CCD
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2014)
 $T_{\min} = 0.601$, $T_{\max} = 0.746$

32729 measured reflections
 1357 independent reflections
 1263 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.074$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.048$
 $S = 0.81$
 1357 reflections
 81 parameters
 3 restraints
 H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.43$ e Å⁻³
 Absolute structure: Flack x determined from 486 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons & Flack, 2004)
 Absolute structure parameter: 0.011 (8)

Table 1

Hydrogen-bond geometry (Å, °).

$\text{D} \cdots \text{H} \cdots \text{A}$	$\text{D} \cdots \text{H}$	$\text{H} \cdots \text{A}$	$\text{D} \cdots \text{A}$	$\text{D} - \text{H} \cdots \text{A}$
$\text{O1} - \text{H1} \cdots \text{O1}^1$	0.86 (1)	1.59 (1)	2.445 (2)	172 (4)
$\text{N1} - \text{H1A} \cdots \text{O2}$	0.98	2.09	3.042 (3)	163

Symmetry code: (i) $y, x, -z + 1$.

Data collection: APEX2 (Bruker, 2012); cell refinement: SAINT (Bruker, 2012); data reduction: SAINT (Bruker, 2012); program(s) used to solve structure: olex2.solve (Bourhis *et al.*, 2015); program(s)

used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Acknowledgements

The authors thank Professor Jesper Bendix for help with the graphics for the Scheme.

Supporting information for this paper is available from the IUCr electronic archives (Reference: CV5501).

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supporting information

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Crystal structure of trihydrogen bis[[1,1,1-tris(2-oxidoethylaminomethyl)-ethane]cobalt(III)} trinitrate

Waqas Sethi, Heini V. Johannesen, Thorbjørn J. Morsing, Stergios Piligkos and Høgne Weihe

S1. Comment

We present here a new hexadentate ligand which, when coordinated to a metal center, facilitates dimer formation through H-bonding (Fig. 1, Table 1). This type of structural motif is rare, but some examples exist in the literature, for example *cis*-aqua-hydroxo complexes of chromium(III) (Ardon *et al.*, 1987).

The ligand, 1,1,1-tris(2-hydroxyethylaminomethyl)ethane, is synthesized from 1,1,1-tris (bromomethyl)ethane and ethanolamine and purified by distillation and column chromatography producing the trihydrochloride. Reaction of a suitable metal salt such as $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and oxidation with hydrogen peroxide affords the title compound (the nitrate salt is much less soluble than the chloride salt).

The title compound, large pink hexagonal single crystals, crystallizes in the trigonal space group $R\bar{3}2$ with the Co—Co axis along the trigonal axis. The compound synthesized is racemic, but upon crystallization it resolves spontaneously to produce a racemic conglomerate. The crystal mounted contains the Δ -form as indicated by a Flack parameter of 0.011 (8) (if the structure is inverted, R1 doubles).

The coordination geometry around the Co ions are close to octahedral with the Co1—N1 distance being 1.95111 (18) Å and the Co1—O1 distance being 1.9314 (14) Å. The O1—Co1—O1 angles are 91.01 (6) ° and the N1—Co1—N1 angles are 92.38 (7) °. The three bridging H-atoms could not be completely located in the Fourier map and were added with a riding model. However, because of the high symmetry and disorder, six equivalent H atom positions exist with the occupancies fixed to 0.5. *ORTEP* plot in Fig. 1 shows all six possible positions. Solving the structure in a space group of lower symmetry does not resolve three H atoms in the trigonal prism formed by the six oxygen atoms, and we take this as a sign that the three H-atoms are disordered over the six positions. The Co—Co distance in the dimer, which is of interest in regards to future analogues with paramagnetic metal ions, is 4.607 (2) Å. This could give interesting magnetic characteristics for the metal ions like Cr(III) and Mn(III).

S2. Experimental

Synthesis of the ligand: 1,1,1-tris(bromomethyl)- ethane (60 g, 0,20 mol) was dissolved in ethanolamine (200 ml, 3,3 mol) in a flask fitted with a condenser and a nitrogen in and outlet. After the system was flushed with nitrogen 10–15 min. the mixture was refluxed (170 °C) for 4 h under continued nitrogen flow. The result is a clear pale yellow oil. To remove surplus ethanolamine the reaction mixture was azeotropically distilled using Chlorobenzene (b.p. at approx. 128 °C). After approximately one week ethanolamonium bromide crystallizes and can be removed by filtration. The resulting oil was dissolved in 1M HCl is put on a cation exchange column (AG 50 W-X2 cation exchange resin (H⁺form), 5x50cm) and washed with copious amounts of water. The column is then eleuted with 1M HCl followed by 2M HCl to remove excess ethanolamine. Finally, the column was eluted with 3M HCl to isolate the product. The 3M HCl eluate was evaporated to dryness to get the product as the hydrochloride salt (an oil). The yield was around 40–50%. ¹H NMR

(D₂O): δ = 1.03 (3 H, $-\text{CH}_3$), 2.94 (6 H, $\{-\text{CH}_2\}_3$), 3.05 (6 H, $\{-\text{CH}_2\}_3$), 3.52 (6 H, $\{-\text{CH}_2\}_3$) p.p.m..

$\text{C}_{11}\text{H}_{24}\text{N}_3\text{O}_3 \cdot 3\text{HCl} \cdot 10\text{H}_2\text{O}$ (535.9): calcd. C 24.65, N 7.84; found C 24.88, N 7.91.

Synthesis of the title compound: 3 g (10 mmol) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 10 ml water. 5 g (10 mmol) $\text{CH}_3\text{C}(\text{CH}_2\text{NHC}_2\text{H}_4\text{OH})_3 \cdot 3\text{HCl} \cdot 10\text{H}_2\text{O}$ is dissolved in 10 ml water and added dropwise to the CoII solution. 0.6 g (6 mmol) trimethylamine is also added to the reaction mixture. Concentrated H_2O_2 is added dropwise to the reaction mixture until a red powder precipitates. The red powder can be recrystallized from water. Yield: 1.77 g (45%). $\text{Co}_2\text{H}_{45}\text{C}_{22}\text{N}_9\text{O}_{15}$ (793.518): calcd. C 33.30, N 15.89; found C 33.31, N 15.07.

S3. Refinement

H atoms were geometrically positioned and refined as riding. The hydroxy atom H1 was placed in the calculated position with occupancy fixed to 1/2, and refined with bond restraint of $\text{O}-\text{H} = 0.87$ (1) Å.

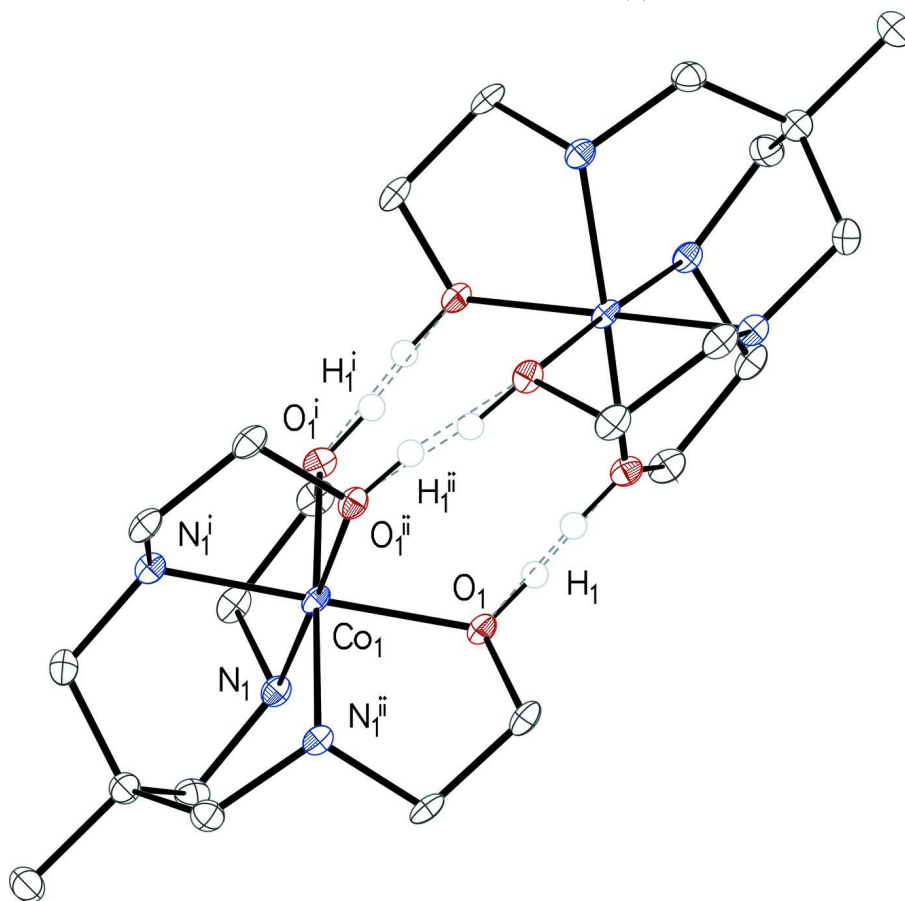


Figure 1

The molecular structure of the dimer cation showing the atomic labels for non-carbon atoms and 50% probability displacement ellipsoids [symmetry codes: (i) $-y, x - y, z$; (ii) $-x + y, -x, z$]. H atoms have been removed for clarity, except for the bridging hydroxy H atoms, each of which is disordered over two positions. Dashed lines denote hydrogen bonds.

Trihydrogen bis{[1,1,1-tris(2-oxidoethylaminomethyl)ethane]cobalt(III)} trinitrate

Crystal data

[Co₂(C₁₁H_{25.5}N₃O₃)₂](NO₃)₃ $M_r = 799.57$ Trigonal, $R\bar{3}2$ $a = 8.543$ (4) Å $c = 39.11$ (2) Å $V = 2472$ (3) Å³ $Z = 3$ $F(000) = 1260$ $D_x = 1.611$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6958 reflections

 $\theta = 2.8$ – 28.1° $\mu = 1.09$ mm⁻¹ $T = 122$ K

Prism, pink

 $0.31 \times 0.25 \times 0.15$ mm

Data collection

Bruker APEXII CCD

diffractometer

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

 $T_{\min} = 0.601$, $T_{\max} = 0.746$

32729 measured reflections

1357 independent reflections

1263 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.074$ $\theta_{\max} = 28.1^\circ$, $\theta_{\min} = 2.8^\circ$ $h = -11 \rightarrow 11$ $k = -11 \rightarrow 11$ $l = -50 \rightarrow 51$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.021$ $wR(F^2) = 0.048$ $S = 0.81$

1357 reflections

81 parameters

3 restraints

Primary atom site location: iterative

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.003$ $\Delta\rho_{\max} = 0.24$ e Å⁻³ $\Delta\rho_{\min} = -0.43$ e Å⁻³Absolute structure: Flack x determined from486 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons & Flack, 2004)

Absolute structure parameter: 0.011 (8)

Special details

Experimental. Absorption correction: *SADABS2014/3* (Bruker, 2014) was used for absorption correction. $wR2(\text{int})$ was 0.1434 before and 0.0855 after correction. The Ratio of minimum to maximum transmission is 0.8053. The $\lambda/2$ correction factor is Not present.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.0000	0.0000	0.55889 (2)	0.00936 (12)	
O1	0.17219 (17)	0.19761 (18)	0.53088 (3)	0.0118 (3)	
H1	0.176 (5)	0.194 (3)	0.5089 (3)	0.018*	0.5
C5	0.0000	0.0000	0.67637 (7)	0.0177 (7)	
N2	0.6667	0.3333	0.57385 (6)	0.0116 (5)	
O2	0.54318 (19)	0.3734 (2)	0.57427 (4)	0.0237 (4)	
C3	0.1892 (3)	0.0424 (3)	0.62458 (4)	0.0143 (4)	

H3A	0.2763	0.1666	0.6304	0.017*
H3B	0.2231	−0.0352	0.6367	0.017*
N1	0.1977 (2)	0.0158 (2)	0.58647 (4)	0.0115 (3)
H1A	0.3088	0.1208	0.5781	0.014*
C2	0.2123 (3)	−0.1482 (3)	0.57812 (4)	0.0133 (4)
H2A	0.1193	−0.2535	0.5900	0.016*
H2B	0.3295	−0.1298	0.5849	0.016*
C4	0.0000	0.0000	0.63662 (7)	0.0130 (6)
C1	0.1742 (4)	0.3620 (2)	0.53957 (4)	0.0144 (4)
H1B	0.0776	0.3682	0.5278	0.017*
H1C	0.2885	0.4659	0.5330	0.017*
N3	0.3333	0.6667	0.6667	0.0389 (11)
O3	0.3333	0.5219 (4)	0.6667	0.0790 (12)
H5	−0.123 (2)	−0.032 (3)	0.6841 (4)	0.008 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.00673 (14)	0.00673 (14)	0.01463 (19)	0.00336 (7)	0.000	0.000
O1	0.0113 (7)	0.0081 (7)	0.0151 (6)	0.0042 (6)	0.0011 (5)	0.0002 (5)
C5	0.0201 (11)	0.0201 (11)	0.0129 (14)	0.0100 (6)	0.000	0.000
N2	0.0084 (8)	0.0084 (8)	0.0180 (11)	0.0042 (4)	0.000	0.000
O2	0.0130 (8)	0.0180 (9)	0.0423 (8)	0.0095 (8)	−0.0007 (6)	0.0011 (6)
C3	0.0134 (10)	0.0152 (10)	0.0144 (8)	0.0072 (8)	−0.0034 (7)	−0.0018 (7)
N1	0.0107 (9)	0.0098 (8)	0.0146 (7)	0.0055 (7)	0.0000 (6)	0.0003 (6)
C2	0.0104 (11)	0.0115 (11)	0.0213 (9)	0.0081 (10)	−0.0001 (7)	0.0014 (7)
C4	0.0129 (9)	0.0129 (9)	0.0133 (13)	0.0064 (5)	0.000	0.000
C1	0.0145 (12)	0.0071 (8)	0.0211 (8)	0.0050 (10)	0.0012 (9)	0.0014 (6)
N3	0.0359 (18)	0.0359 (18)	0.045 (3)	0.0179 (9)	0.000	0.000
O3	0.087 (3)	0.0450 (14)	0.119 (3)	0.0435 (14)	−0.060 (2)	−0.0300 (10)

Geometric parameters (Å, °)

Co1—O1 ⁱ	1.9313 (14)	C3—N1	1.515 (2)
Co1—O1 ⁱⁱ	1.9313 (14)	C3—C4	1.543 (2)
Co1—O1	1.9314 (15)	N1—H1A	0.9800
Co1—N1	1.9511 (17)	N1—C2	1.503 (3)
Co1—N1 ⁱⁱ	1.9511 (18)	C2—H2A	0.9700
Co1—N1 ⁱ	1.9511 (17)	C2—H2B	0.9700
O1—H1	0.861 (12)	C2—C1 ⁱⁱ	1.523 (2)
O1—C1	1.436 (2)	C4—C3 ⁱⁱ	1.543 (2)
C5—C4	1.555 (4)	C4—C3 ⁱ	1.543 (2)
C5—H5	0.987 (18)	C1—C2 ⁱ	1.523 (2)
N2—O2	1.2612 (16)	C1—H1B	0.9700
N2—O2 ⁱⁱⁱ	1.2612 (16)	C1—H1C	0.9700
N2—O2 ^{iv}	1.2612 (16)	N3—O3 ^v	1.237 (3)
C3—H3A	0.9700	N3—O3	1.237 (3)
C3—H3B	0.9700	N3—O3 ^{vi}	1.237 (3)

O1 ⁱ —Co1—O1 ⁱⁱ	91.01 (6)	Co1—N1—H1A	106.7
O1 ⁱ —Co1—O1	91.01 (6)	C3—N1—Co1	116.71 (12)
O1 ⁱⁱ —Co1—O1	91.01 (6)	C3—N1—H1A	106.7
O1 ⁱ —Co1—N1 ⁱ	89.92 (7)	C2—N1—Co1	106.72 (11)
O1—Co1—N1 ⁱⁱ	177.58 (6)	C2—N1—C3	112.72 (14)
O1—Co1—N1 ⁱ	86.74 (7)	C2—N1—H1A	106.7
O1 ⁱⁱ —Co1—N1 ⁱ	177.58 (7)	N1—C2—H2A	110.5
O1 ⁱ —Co1—N1	177.58 (7)	N1—C2—H2B	110.5
O1 ⁱⁱ —Co1—N1 ⁱⁱ	89.92 (7)	N1—C2—C1 ⁱⁱ	106.35 (14)
O1 ⁱⁱ —Co1—N1	86.74 (7)	H2A—C2—H2B	108.7
O1—Co1—N1	89.92 (7)	C1 ⁱⁱ —C2—H2A	110.5
O1 ⁱ —Co1—N1 ⁱⁱ	86.74 (7)	C1 ⁱⁱ —C2—H2B	110.5
N1—Co1—N1 ⁱⁱ	92.37 (7)	C3—C4—C5	107.78 (11)
N1—Co1—N1 ⁱ	92.37 (7)	C3 ⁱ —C4—C5	107.78 (11)
N1 ⁱ —Co1—N1 ⁱⁱ	92.37 (7)	C3 ⁱⁱ —C4—C5	107.78 (11)
Co1—O1—H1	124.2 (19)	C3—C4—C3 ⁱ	111.11 (11)
C1—O1—Co1	110.61 (11)	C3 ⁱⁱ —C4—C3 ⁱ	111.11 (11)
C1—O1—H1	107 (2)	C3 ⁱⁱ —C4—C3	111.11 (11)
C4—C5—H5	107.8 (10)	O1—C1—C2 ⁱ	107.19 (14)
O2 ⁱⁱⁱ —N2—O2	119.982 (8)	O1—C1—H1B	110.3
O2 ^{iv} —N2—O2	119.984 (8)	O1—C1—H1C	110.3
O2 ⁱⁱⁱ —N2—O2 ^{iv}	119.983 (8)	C2 ⁱ —C1—H1B	110.3
H3A—C3—H3B	107.8	C2 ⁱ —C1—H1C	110.3
N1—C3—H3A	109.0	H1B—C1—H1C	108.5
N1—C3—H3B	109.0	O3 ^v —N3—O3 ^{vi}	120.000 (3)
N1—C3—C4	112.85 (16)	O3 ^{vi} —N3—O3	119.999 (4)
C4—C3—H3A	109.0	O3 ^v —N3—O3	120.001 (9)
C4—C3—H3B	109.0		
Co1—O1—C1—C2 ⁱ	36.7 (2)	N1—C3—C4—C3 ⁱ	−71.71 (18)
Co1—N1—C2—C1 ⁱⁱ	41.38 (17)	N1—C3—C4—C3 ⁱⁱ	52.55 (19)
C3—N1—C2—C1 ⁱⁱ	170.77 (17)	C4—C3—N1—Co1	16.05 (19)
N1—C3—C4—C5	170.42 (11)	C4—C3—N1—C2	−108.00 (16)

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $-y+1, x-y, z$; (iv) $-x+y+1, -x+1, z$; (v) $-x+y, -x+1, z$; (vi) $-y+1, x-y+1, z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O1 ^{vii}	0.86 (1)	1.59 (1)	2.445 (2)	172 (4)
N1—H1A \cdots O2	0.98	2.09	3.042 (3)	163

Symmetry code: (vii) $y, x, -z+1$.